SURFACE TENSION EFFECTS ON PROPERTIES OF COAL SUSPENSIONS

Principal Investigator: Dr. A.W. Neumann

CONTRACT SERIAL NO. OST84-00513
CONTRACTOR: University of Toronto

Final Report for EMR Contract

24ST.23440-4-9162

on

Surface Tension Effects on Properties of Coal Suspensions

Principal Investigator: Dr. A.W. Neumann

September 1985

University of Toronto
Department of Mechanical Engineering
5 King's College Road
Toronto, Ontario
M5S 1A4

35pp

TABLE OF CONTENTS:

		PAGE
A.	FOCUS	2
B.	SUMMARY OF METHODOLOGY	2
C.	MATERIALS	3
	C.1. Coals	3
	C.2. Surfactants	3
D.	RESULTS	5
	D.1. Measurements of Surfactant Adsorption to Coal	5
	D.2. Effect of Surfactant Adsorption on the Surface Properties of Coal Particles	5
	D.2.1. Pittsburgh No. 8 coal	6
	D.2.2. Devco coal	7
E.	CONCLUSIONS	8
F.	DETAILED DESCRIPTION OF METHODOLOGY	8
	F.1. Surfactant Adsorption	8
	F.2. Sedimentation Volume Studies	10
TABLES 1-3		11-13
FIGURES 1-10		14-23

A. FOCUS

This study was designed to answer four principal questions:

1. Do surfactants adsorb irreversibly onto coal fines?
2. Is the extent of adsorption to one and the same coal sample primarily determined by the charge or by the molecular weight features of the surfactant?
3. Does surfactant adsorption change the wettability of the coated coal particles?
4. Does surfactant adsorption affect the packing nature of the coal slurry?

B. SUMMARY OF METHODOLOGY

In order to address these questions, the following methods were employed (experimental details are given in Section F).

1. Extent of surfactant adsorption to a given unit mass of coal was assessed spectrophotometrically by means of standard curves using the ultraviolet adsorption maxima of each surfactant (cf. Section F/1).
2. The effect of surfactant charge and molecular weight properties was investigated by deliberately choosing various surfactants having different properties.
3. The wettability of surfactant coated and uncoated coal fines was determined by means of sedimentation volume studies. (Section F/2).

4. The effect of surfactant coating on coal slurries was examined in two ways:

   a) qualitatively by determining visually the ease with which a compacted slurry could be resuspended; and

   b) quantitatively by assessing with image analysis techniques the change in size of coal particle aggregate formation as a result of surfactant coating.

C. MATERIALS

C.1. Coal Samples

Two bituminous coal samples were employed in this study:

a) Pittsburgh coal #8

b) Devco

For both samples the coal particle size was -400 mesh. The ultimate and proximate analysis for the samples is given in Table 1.

C.2. Surfactants

The following surfactants were employed in the study:

a) Dispersant A-23,
   Diamond Chemical Company,
   Morristown, N.J.
   (anionic)

b) Tween 20 (Polyoxyethylene sorbitan monolaurate)
Polysciences Inc., Warrington, P.A.
(nonionic)

c) Triton X-100 (Octyl Phenoxy Polyethoxyethanol)
Fisher Scientific Co.,
Toronto
(nonionic)

d) Substituted Ethoxylated Phenylsulfonamides
(specially prepared for us by USDA,
Philadelphia by courtesy of Dr. R.A. Barford).

Structure: $C_4H_9O\ SO_2N<^{R'}_{(CH_2CH_2O)_{20}H}$

$R' - C_{10}H_{21}$

Molecular weight: $\cong$ 1200

e) High molecular weight plant cell membrane extract. This material was extracted from wheat husks at pH 7. It is a linear hemicellulose polymer chain with the individual units linked together through β 1,2 glycosidic linkages. The molecular weight of the extract is unknown at this time. The surface tension of this material was determined by means of contact angle measurements on layers of the polymer deposited by pressure ultra-filtration on anisotropic cellulose acetate membranes. From the contact angle value determined at the plateau region, as shown in Figure 1, it is possible, using an equation of state approach, to determine the surface tension of this material.

D. RESULTS

D.1. Measurements of Surfactant Adsorption to Coal

This study was performed using a low molecular weight (LMW) surfactant (Triton X-100, MW ≅ 700) and Devco coal only. For this purpose, the kinetics of the extent of surfactant adsorption (cf. Section F/1) was determined for two bulk concentrations of Triton X-100. The bulk concentrations examined were 0.2 mg/ml and 3.2 mg/ml. Surfactant adsorption was monitored from 30 minutes to 180 minutes.

The results shown in Figure 2 indicate that surfactant adsorption occurred rapidly and that saturation had occurred by 30 minutes. Extensive dilution studies revealed that Tween 20 adsorption to coal was irreversible. The extent of adsorption appeared to be bulk concentration dependent, in that a 2-fold increase in the amount adsorbed per unit mass occurred when the concentration was increased from 0.2 to 3.2 mg/ml.

D.2. Effect of Surfactant Adsorption on the Surface Properties of Coal Particles

Surface properties of coal particles pre-coated by treatment with surfactants were investigated. The concentration of the surfactants was 0.2% in all cases. The following surfactants:

0.2% (w/v) A-23 (anionic)

0.2% (w/v) Tween 20 (nonionic)

0.2% (w/v) Triton X-100 (nonionic) and

one high molecular weight surface active material (Plant cell cellulose) were employed. Two coal samples (Pittsburgh #8 and Devco) were studied.

The surface tension of the surfactant-coated coal particles was determined by means of sedimentation volume studies (cf. Section F/2).

D.2.1. Pittsburgh Coal #8

Sedimentation experiments with pretreated coal fines were performed in the n-propanol/water mixtures. The fines were precoated in 0.2% aqueous solutions. In cases where two surfactants were used, pretreatment was performed with solution containing 0.2% of each surfactant.

The results of this study are summarized in Table 2 and illustrated in Figures 3-8. It is obvious that the adsorption of the LMW surfactants changes considerably the surface tension, γ_{PV}, (being equal to γ_{LV} at sedimentation) of the coal particles. The anionic A-23 dispersant lowers the surface tension of the coated coal particles by about 12 ergs/cm^2 (Fig. 5), whereas the nonionic surfactant (Tween 20) lowers the surface tension by about 5 ergs/cm^2 (Fig. 6).

In addition, a striking synergistic effect was noted when the coal was treated with both LMW surfactant plus the plant cell hemicellulose material (PCC). In the case of A-23 + PCC, this combination leads to the production of coal particles with a surface tension of $\cong$ 47.0 ergs/cm^2 (cf. Figure 7, Table 2). In the case of Tween 20 + PCC, no such synergistic increase in surface tension was noted (cf. Figure 8, Table 2).

In addition to the differences in surface tension of the coated particles as described above, differences in the nature of the slurry of the treated coal were also observed.

In the case of A-23, the resultant coal slurry was relatively stable and was easy to disperse over long periods of time (3 months). In contrast, the Tween 20 treated coal gave rise to a slurry which became extremely solid and very difficult to resuspend. Compaction occurred rapidly - often within 30 hours.

D.2.2. Devco Coal

In this study the surface tension of Devco Coal coated with the nonionic Triton X-100 was determined by means of sedimentation volume studies. Two bulk concentrations were examined: 0.2 mg/ml and 3.2 mg/ml. The results of this study are shown in Figure 9. The lower concentration resulted in a lowering of the coal surface tension of $\cong$ 1 erg/cm^2, whereas the higher concentration resulted in a lowering in the coal surface tension by about 11 ergs/cm^2.

Surfactant (Triton X-100) coating of Devco coal produced, at both bulk concentrations, coal slurries which were notably more stable. This statement is made based on the observation that over extended periods (60 days) the surfactant treated slurry was much easier to resuspend than the uncoated coal slurry. The latter compacted rapidly and by day 10 was already difficult to resuspend.

Extensive dilution studies (21 days) revealed that Triton X-100 adsorption was irreversible.

E. CONCLUSIONS

1. Surfactant adsorption to coal occurs rapidly and is irreversible.
2. Surfactant adsorption decreases the surface tension of the coated coal particles.
3. The amount of the adsorbed surfactant to a unit mass of coal is determined in part by the bulk concentration of the surfactant: the adsorbed amount increases with increasing bulk concentration.
4. The amount of surfactant adsorbed per unit mass of coal decreases the surface tension of the coated coal particles.
5. Surfactant adsorption changes the nature of the coal slurry. The nature of this change is dependent both on the character of the adsorbing surfactant and on the surface concentration of the adsorbed surfactant.

F. DETAILED DESCRIPTION OF METHODOLOGY

F.1. Surfactant Adsorption

The extent of surfactant adsorption to a fixed mass of coal was determined as follows:

a) Setting-up Standard Curves

Triton X-100 has an ultraviolet absorption maximum at 224 nm. Thus, a standard curve of UV absorbance vs. surfactant bulk concentration was established. This was linear in the

concentration range examined as shown in Figure 10. Having thus established this reference curve, any subsequent absorbance value measured at 224 nm could be used to determine the unknown concentration of a surfactant solution.

b) Surfactant Adsorption

1. 0.1 gram of coal (-400 mesh) was weighed with analytical accuracy into Micro test tubes (1.5 ml capacity).

2. To each tube 1 ml of surfactant solution at the desired bulk concentration was added. Thereafter, the tubes were capped and sealed.

3. The coal suspension was then incubated on a rotary mixer (to ensure complete mixing) for the desired incubation period.

4. Thereafter, the tubes were centrifuged to pellet the coal particles and the supernatant was removed.

5. The coal particles were then resuspended in 1 ml of deionized and distilled water and washed by centrifugation 5 times in this manner in order to remove any non-adherent surfactant molecules.

6. All supernatants were diluted to a suitable known volume. The surfactant solution was then placed in a spectrophotometer in order to determine the solutions UV absorbance. Following the appropriate volume correction, the concentration of the surfactant in the pooled supernatant was then determined. Hence, since the original amount of surfactant and the amount remaining in solution following incubation with the coal were known, it was thus possible to determine through

the difference, the amount of surfactant which was adsorbed onto a fixed mass of coal.

Controls: 1) UV Absorbance values should be determined for each surfactant concentration employed, by placing 1 ml of these solutions in microtubes containing no coal. This allows one to take into account the amount of surfactant adsorption onto the walls of the reaction vessel, thereby enhancing the accuracy of the data.

2) Following each incubation in the presence of coal, the supernatant should be scanned from 210-260 nm to ensure that any organics that leach out of the coal are not contributing to the 224 nm reading. This is easily detected by changes in the profile of the 210-260 scan. If such changes are detected care must be taken to determine quantitatively the extent of such contributions, which should then be taken into account.

In order to determine the irreversibility of surfactant adsorption, the following procedure was followed:

After rinsing the coal samples, the particles were resuspended daily in fresh aliquots of distilled water. In each case the supernatant that was removed was assayed for surfactant concentration by means of UV absorbance studies.

F.2. Sedimentation volume studies

The technical details of this technique have been described previously. Details are given in the attached reprint. For the present studies the required liquid surface tensions were produced in all cases through binary mixtures of n-propanol and water. The range in liquid surface tensions produced in this way are given in Table 3.

TABLE 1

Proximate and Ultimate Analysis Data for the -400 Mesh Fractions of Pittsburgh No. 8 and Devco Coals (as received).

Coal Sample	Proximate analysis				Ultimate analysis				
	Moisture	Ash	Volatile	Fixed carbon (diff.)	C	H	N	S (total)	O (diff.)
	(wt%)				(wt%)				
Pittsburgh No. 8	2.41	6.43	35.58	55.58	76.84	5.52	1.59	1.36	5.83
Devco	1.03	2.78	34.60	61.59	85.00	5.23	1.54	0.88	3.54

TABLE 2

Surface Tensions of the Pretreated Coal Particles as Determined by Sedimentation Volumes in n-Propanol/Water Mixtures.

Coal sample	Additives		Surface tension
	Type	Concentration (mg/ml)	(ergs/cm^2)
Pittsburgh No. 8	none (untreated)		36.5
	A-23	0.2	24.2
	Tween 20	0.2	31.2
	A-23 + PCC	0.2	47.5
	Tween 20+PCC	0.2	30.7
Devco	none (untreated)		69.0
	Triton X-100	0.2	68.0
	Triton X-100	3.2	58.0

TABLE 3

Surface Tension, γ_{LV}, of n-Propanol/Water Liquid Pairs Used for Untreated and Pretreated Coal Sedimentation at 20°C.

Mixtures used for Untreated coal				Mixtures used for Pretreated coal	
Propanol (vol %)	γ_{LV} (ergs/cm^2)	Propanol (vol %)	γ_{LV} (ergs/cm^2)	Propanol (vol %)	γ_{LV} (ergs/cm^2)
100	23.8	2	53.8	100	23.6
80	25.0	1	55.2	95	24.2
60	25.6	0.8	58.0	90	24.5
50	26.0	0.6	60.4	85	24.7
40	26.3	0.4	63.3	80	24.8
30	27.0	0.3	66.1	75	25.1
25	28.2	0.2	68.1	70	25.2
20	30.3	0.1	70.8	65	25.3
18	31.3	0	72.8	60	25.5
16	32.9			55	25.7
14	34.2			50	25.8
12	36.5			30	27.1
10	38.0			20	30.5
9	38.8			15	33.3
8	40.1			10	38.8
7	41.3			5	48.6
6	43.2			2.5	56.2
5	44.7			1.0	63.9
4	46.5			0.5	67.8
3	49.4			0.1	71.5

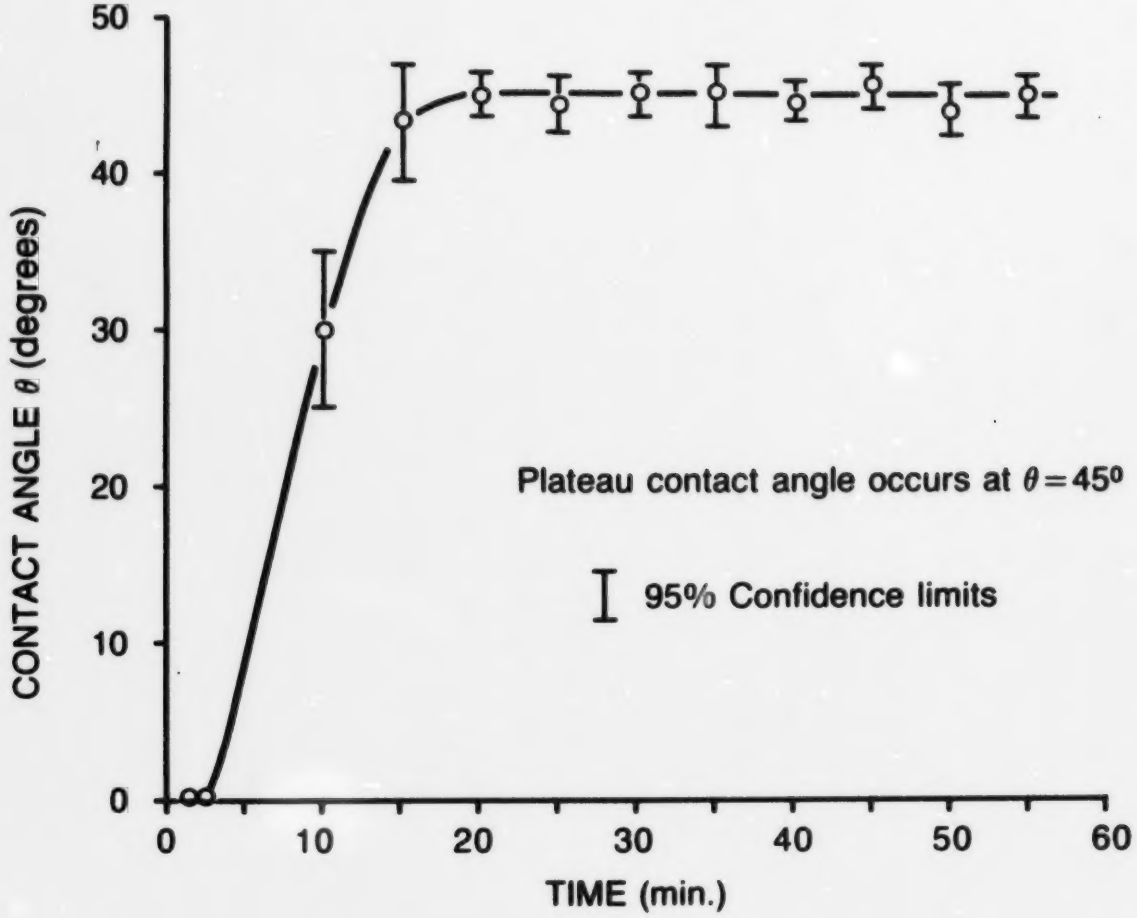

Figure 1 Contact angles with water on layers of PCC material as a function of time.

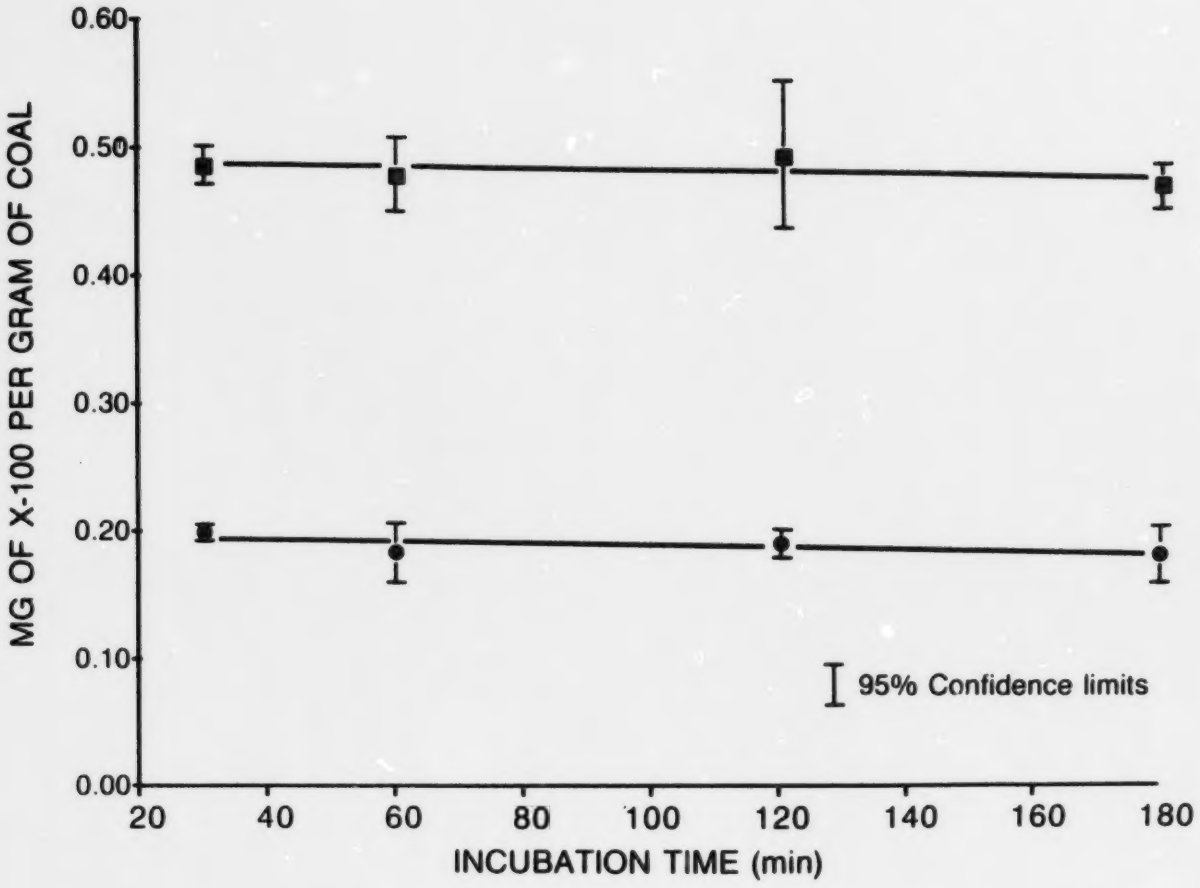

Figure 2 Adsorbance of Triton X-100 (0.2 and 3.2 mg/ml) to Devco coal (-400 mesh).

Figure 3 Photomicrograph illustrating the sedimentation volume technique as applied to Pittsburgh coal No. 8 in n-propanol/water liquid mixtures.

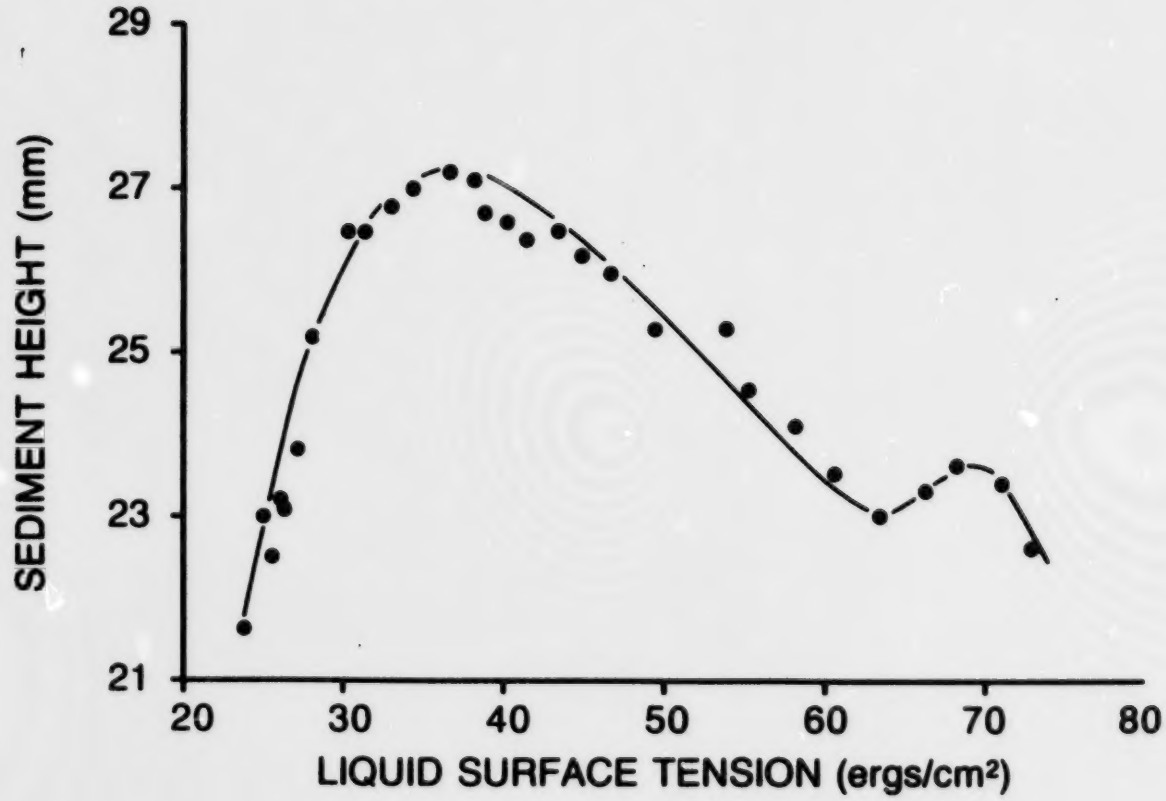

Figure 4 Sedimentation volume (as measured by its height) as a function of the surface tension, γ_{LV}, of the suspending liquid (n-propanol/water) for untreated Pittsburgh coal No. 8.

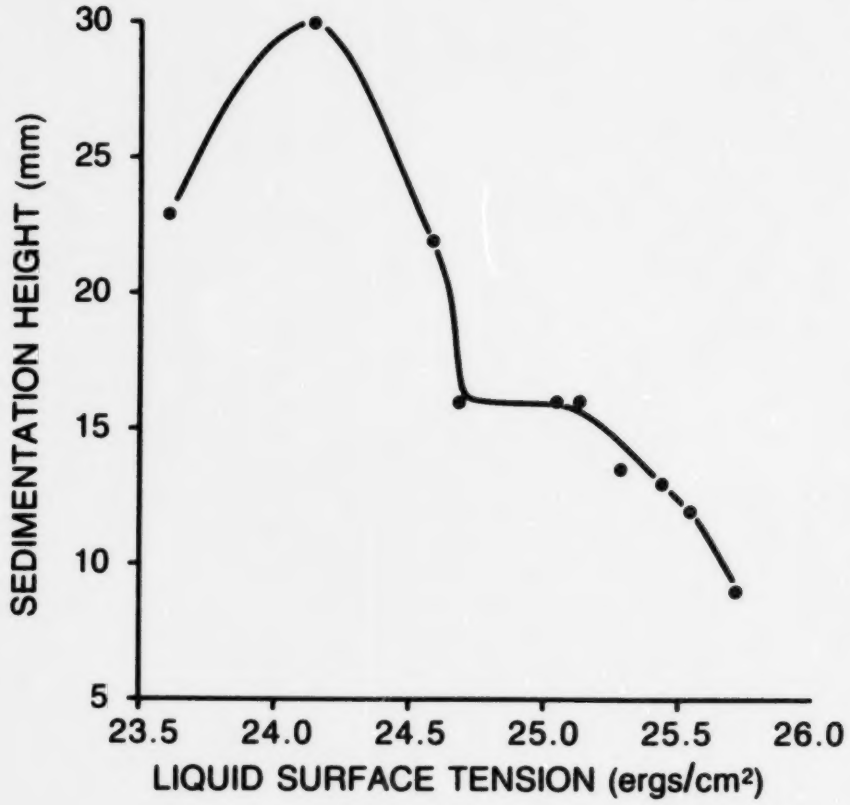

Figure 5 Sedimentation volume (as measured by its height) as a function of the surface tension, γ_{LV}, of the suspending liquid (n-propanol/water) for Pittsburgh coal No. 8 pretreated with 0.2% A-23 surfactant solution.

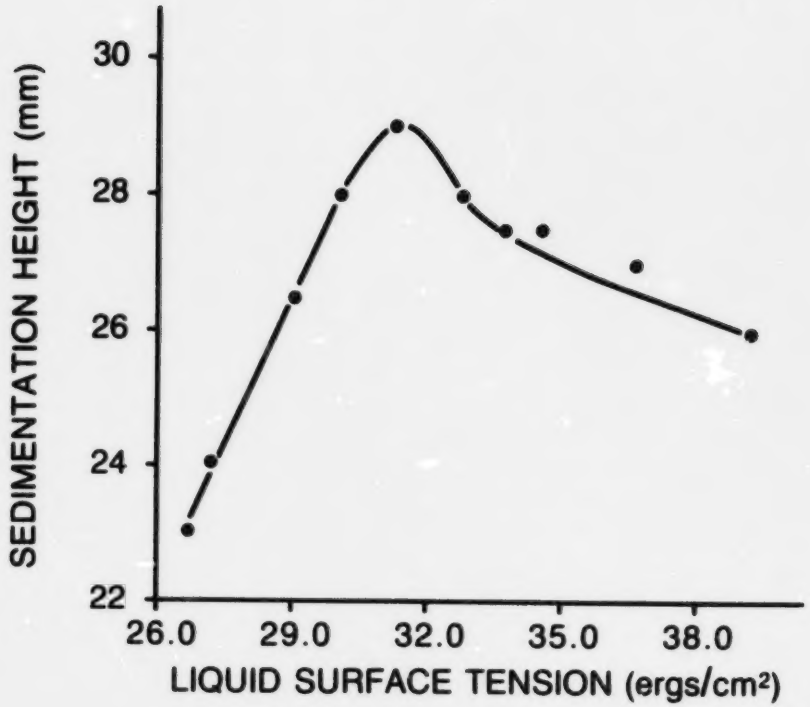

Figure 6 Sedimentation volume (as measured by its height) as a function of the surface tension, γ_{LV}, of the suspending liquid (n-propanol/water) for Pittsburgh coal No. 8 pretreated with 0.2% Tween 20 surfactant solution.

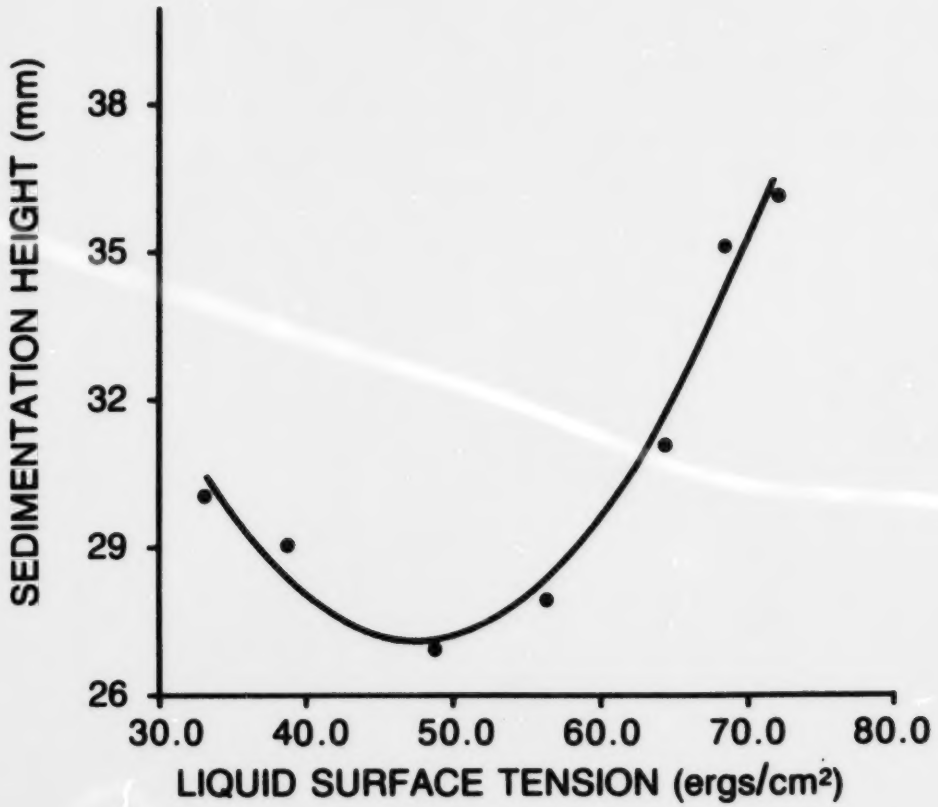

Figure 7 Sedimentation volume (as measured by its height) as a function of the surface tension, γ_{LV}, of the suspending liquid (n-propanol/water) for Pittsburgh coal No. 8 pretreated with a solution of 0.2% A-23 and 0.2% PCC surfactants

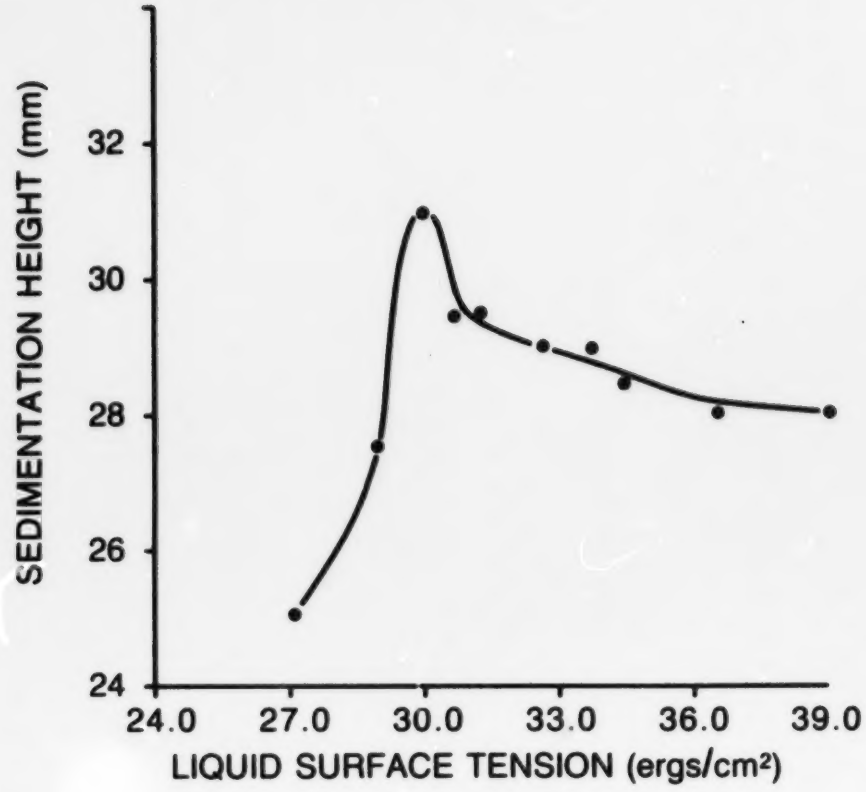

Figure 8 Sedimentation volume (as measured by its height) as a function of the surface tension, γ_{LV}, of the suspending liquid (n-propanol/water) for Pittsburgh coal No. 8 pretreated with a solution of 0.2% Tween 20 and 0.2% PCC surfactants.

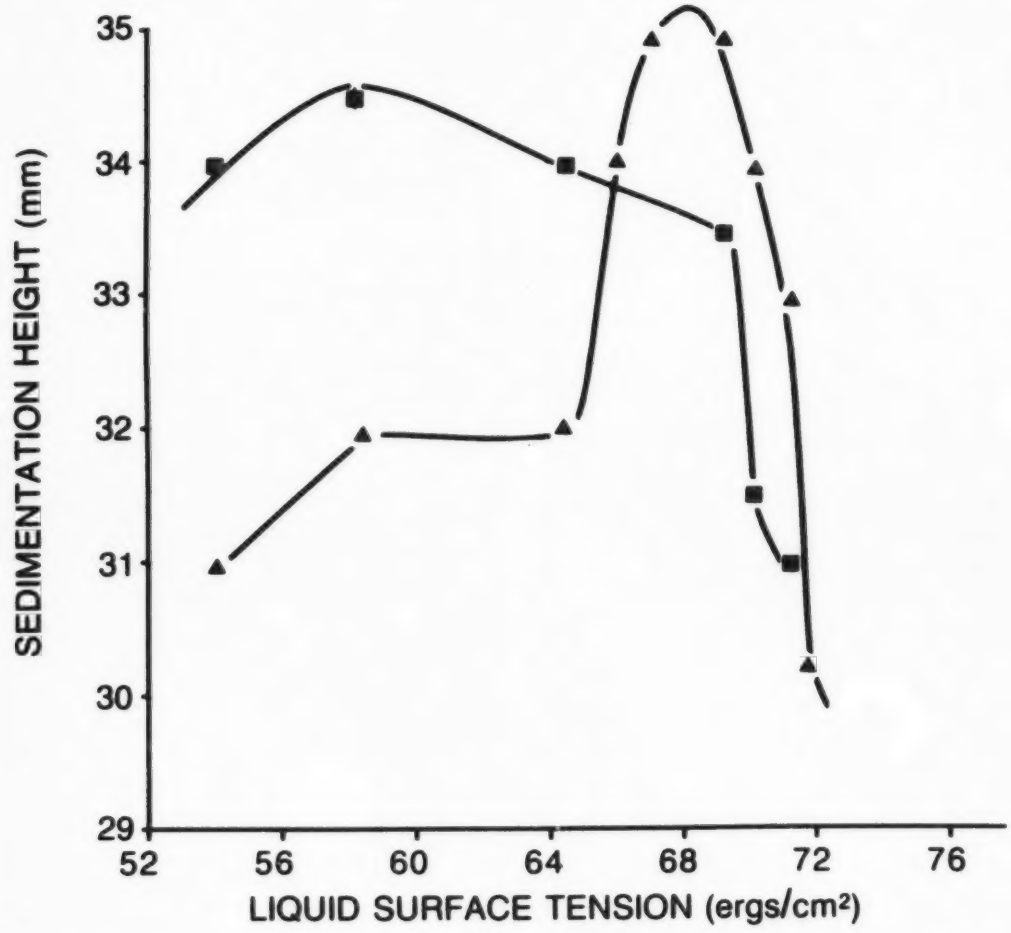

Figure 9 Sedimentation volume (as measured by its height) as a function of the surface tension, γ_{LV}, of the suspending liquid (n-propanol/water) for Devco coal pretreated with Triton X-100 solutions of different bulk concentrations:

o 0.2 mg/ml.

x 3.2 mg/ml.

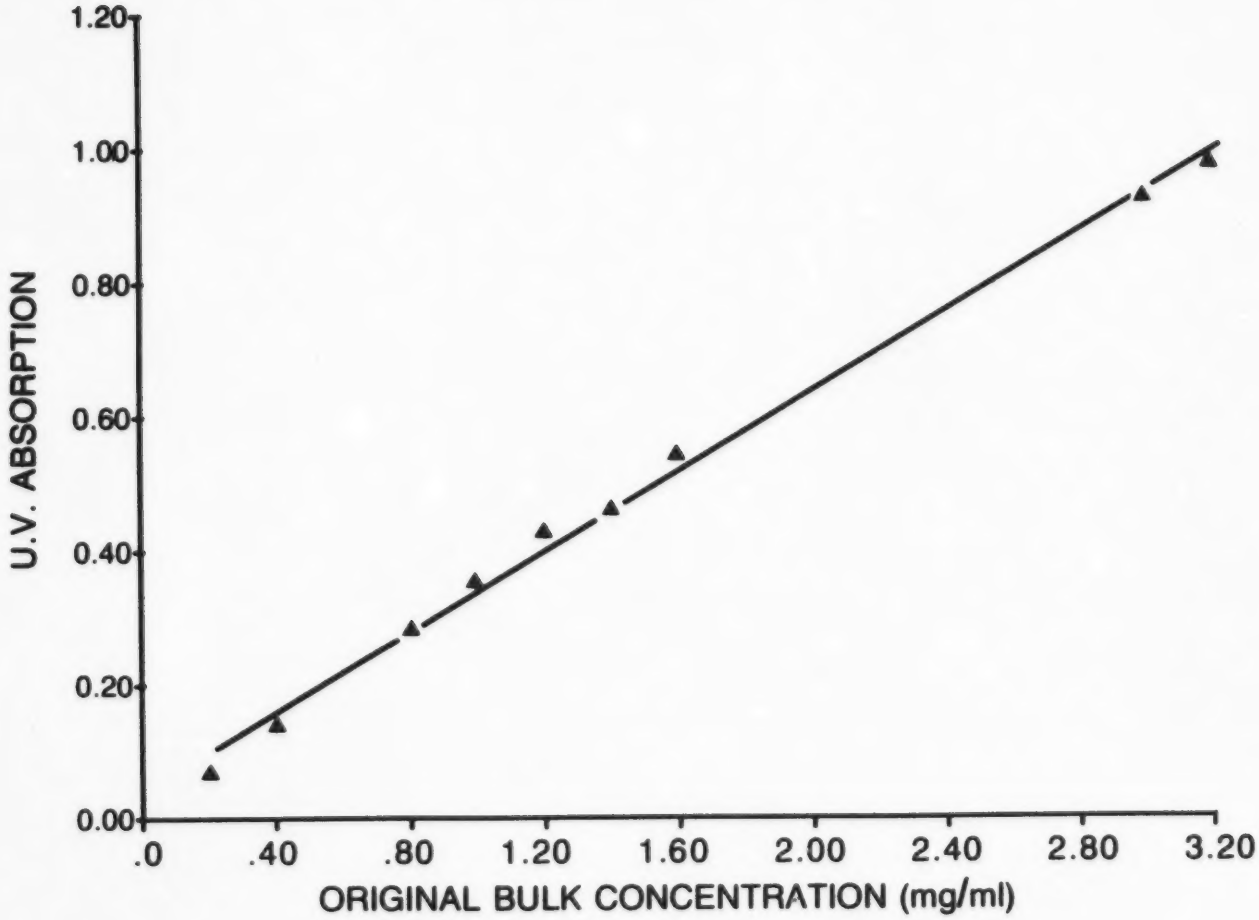

Figure 10 UV absorbance of Triton X-100 as a function of surfactant bulk concentration